GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: March 20, 1978

Project Title: Study of the Charring and Activation of Agricultural Waste Products as a Source of Activated Carbon

Project No: A-2113

Project Director: Stanton B. Smith

Sponsor: Pacific Carbons, Inc.

Agreement Period: From 3/4/78 Until 6/30/78

Type Agreement: P.O.# 144-78-6002

Amount: $5,000

Reports Required: As requested.

Sponsor Contact Person (s):

Technical Matters

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P.O. Box 755
Blue Lake, CA 95525

Contractual Matters
(thru OCA)

Defense Priority Rating:

Assigned to: Technology & Development Laboratory (School/Laboratory)

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GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION SHEET

Date 10/2/81

Project Title: Study of the Charring and Activation of Agricultural Waste Products as a Source of Activated Carbon

Project No: A-2113

Project Director: Stanton B. Smith

Sponsor: Pacific Carbons, Inc.

Effective Termination Date: 12/31/80

Clearance of Accounting Charges: 12/31/80

Grant/Contract Closeout Actions Remaining:

- [x] Final Invoice ~~and Closing Documents~~
- [ ] Final Fiscal Report
- [ ] Final Report of Inventions
- [ ] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other ____________

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FORM OCA 10:781

ENGINEERING EXPERIMENT STATION
GEORGIA INSTITUTE OF TECHNOLOGY • ATLANTA, GEORGIA 30332

November 6, 1980

Mr. Larry E. Davis
Vice President-Marketing
Pacific Carbons Inc.
53 Marblehead Harbor
Bradford Wood, PA 15015

RE: Project No. A-2113

Dear Larry:

We have completed the work covered by your letter of October 18, 1980 and further outlined in several telephone conversations. A scope of somewhat reduced form based on my letter of October 8 has been followed. A letter report completing this work follows.

INTERIM REPORT -- PACIFIC CARBON PEACH PIT PROJECT

BACKGROUND

A thorough study of the charring and activation of crushed and sized peach pits was completed in our laboratory in October 1978 which led to the full scale activation trials at the Pacific Carbons Inc., Blue Lake, California plant. The above study was confined to a fine mesh crushed peach pit and indicated that 12 x 40 mesh carbons of good hardness and density could be produced at acceptable activity levels. Recent emphasis, however, has been on coarser carbons of a final 4 x 10 nominal size. Difficulties have been encountered in obtaining good densities with the coarser particles. The tests outlined below were undertaken and the comparisons were made with data taken from the October 1978 report.

TASK 1

Large samples of both raw crushed peach pits and the char produced from these pits at PCI were sent to us for comparative tests on charring and activation. The problem encountered at PCI was that the densities of the char and the activated product were much lower than those obtained on the lab using a fine-sized crushed pit as reported in our October 1978 report on Project No. A-2113. A laboratory muffle furnace pyrolysis was requested to be compared with the previous fine particle study.

It was also arranged that activations on both the PCI char and that produced in the muffle be carried out. However, after initial results on charring showed close similarity to plant results, it was decided to drop the activation study until reasons for the low initial density could be found.

TASK 1 EXPERIMENTAL WORK

The coarse crushed pits were taken "as received" and charged to the muffle furnace using the same type stainless steel food container with cover as shown in the above-mentioned report. However, this unit had a slightly different geometry with respect to the distributor for the nitrogen purge gas stream and the positioning of the thermocouples. Figure 1 indicates the location of these elements.

Even though the pits were slightly damp it was only possible to charge 3.08 kg as compared to 3.5 kg for the finely ground pits previously studied due to the lower apparent density of 0.589 g/ml. Figure 2 shows the traces for the three thermocouples during the pyrolysis run. The trace for the furnace control couple is not shown but the target termerature was generally reached for s everal minutes before the setting was increased by 50^{o}C every 15 minutes. The pyrolysis was started with a muffle temperature set at 350^{o}C and the temperature was advanced after the first 15 minutes. It took 10 minutes before the temperature of the furnace was felt by the T/C's and 25 minutes before the charge reached boiling water temperature. Drying was not complete until about 55 minutes had elapsed. At that point the heat appeared to penetrate from above as the upper T/C's rose in temperature much faster than the lower #7 T/C. Even after 110 minutes the lower T/C appeared to lag below #8 and #9, but when the furnace was jarred at 125 minutes, so that the char bed settled, then the temperatures came closely in line as the charring was completed. The final temperature setting of 815^{o}C (1500^{o}F) was reached at 130 minutes and the charge finally reached this temperature at 140 minutes. The run was terminated at 160 minutes at which point 1500^{o}F was again reached as the controller cycled to some degree in holding temperature setting. (A final setting of 840^{o}C (1544^{o}F) was made for the last 15 minutes to maintain the final temperature target.)

The charge was removed from the muffle and allowed to cool to room temperature while the nitrogen purge was kept flowing. The product amounted to 863 g and had an AD of .474 g/ml. The yield on original "as received" ground pits was 28% by weight and 34.8% by volume. The data is shown in Table I. Though no moisture determination was made it might be assumed to be around 14% as in the case of the finely ground pits. Using this value to calculate a dry basis yield indicated a yield of 32.6% which is almost identical to the 31.3% db yield on the fine pits.

TASK 2

About a month later in response to a telephone request, work was resumed on activation of PCI char made from coarse-fraction pits charred in the plant kilns. The objectives were to activate this char, after removal of fines (-10 mesh), to two activity levels as determined by iodine number at 900 and 1100 mg/g, resp. Enough of this material was to be made to determine Abrasion No. as well as IN, AD, DI and CCl_4 Capacity. It was later decided in the interest of keeping cost down to carry out multiple activations at only the 900 IN level to enable determination of Abrasion No.

TASK 2 EXPERIMENTAL WORK

The activations of 50 g quantities of the dried +10 mesh PCI char were made using steam alone (2g/min) at a nominal temperature of 1700°F, which was judged best in the fine particle study to give the most efficient CCl_4 capacity development. After referring to the data on fine particle activation it was decided to run two exploratory activations at times selected to give comparable yields for the IN target levels. A 50 minute activation was selected initially since it was expected that the gasification rate would be slower on the larger particles. However, a yield of 49% was obtained which was lower than the 54% expected. A 41 minute time was then selected for the second trial which gave a 59.6% yield. When the IN's were determined they came remarkably close to the target values.

Since four activations would have to be made @ 50 g/charge in order to have sufficient sample for Abrasion No., it was decided to increase the time to 42 minutes so as to put the IN over 900 mg/g. As shown in Table II the expected yield, AD, and IN values were obtained.

After the analyses were completed it appeared that the CCl_4 value for the 42 min composite was a bit low perhaps because it was not given additional drying as the other samples had before testing. However, there was insufficient unused sample for an additional test without running additional activations. It was then decided to use the abraded sample from the hardness test since the abrasion treatment would not affect the equilibrium CCl_4 capacity providing the entire sample, including fines, was used. This sample was dried for over one hour at 140°C and the CCl_4 capacity determined. Though not requested, CCl_4 retentivities were also determined since this is done simply by blowing the samples with air for 6 hours and again determining the weight, which could be done without additional expense.

DISCUSSION OF RESULTS

Task 1, Charring Test

The charring produced a material that was grayer in color and quite a bit cleaner than the plant production. However, that was to be expected since there was no mechanical action in the muffle pyrolysis. Figures 4 and 6 show the density decrease during charring and activation in the lab for both the fine and coarse particles. Though the slopes of the pyrolysis and activation portions of the curves are very different, it is quite evident that the lines are exactly parallel. It is therefore quite clear that one is almost entirely dependent on the density of the raw material in reaching a desirable density in the product.

It is quite evident by visual observation that the large particles have large grooves in the surface as observed on the uncrushed pits themselves. This is not the case with the fine particles which appear to be very much rounded and smooth. This can certainly be one valid reason that coarse pit particles lead to consistently lower densities.

It is also worth pointing out that the PCI char was even slightly more dense than the lab char, however, when corrected for 4.3% moisture the PCI char would be .467 g/ml vs. .474 for the lab char. It is also somewhat surprising that upon drying and removing the -10 mesh fraction the density dropped significantly to .433 g/ml. Thus it appears that the fine particles tend to fill in the voids between larger particles and increase the overall density.

Task 2, Activation Tests

Complete data for Task 2 is given in Table II and Figures 3-8 interpret the data in comparison with corresponding data from the small particle work.

Figure 3 shows the Iodine No. and Decolorizing Index values plotted beside the fine particle data over a wider range of yields. The curves are roughly parallel for both parameters but it is quite striking that the iodine curve shows somewhat lower values for a given yield whereas the DI values are markedly higher. It appears, then, that the larger pores are being developed faster in this char. We cannot say at this point, however, whether the particle size or the pyrolysis conditions are responsible for this difference.

Figure 4 is a similar plot for the Carbon Tetrachloride Capacity and Retentivity data from these samples. In this case the 41 and 50 minute samples appear to be very close to the original fine particle activation curve. However, the Composite 42 min sample gave a much poorer capacity. A rerun of the sample boosted the CCl_4 capacity slightly. It is possible that the first two results are somewhat high as we had just started up the "carbontet" apparatus and were having some trouble with the drying train that might have resulted in over-saturation of the air stream because of low velocity.

In the retentivity data a very great difference from the fine particles is noted. The coarser particles should have a much larger "working capacity" in vapor phase recovery operations. This would tend to bear out the opening up of larger pores in the coarse particles as previously indicated by the higher DI values. It will be interesting to see when the muffle-pyrolyzed char is activated whether finer pores will result.

A comparison of burn-off rate for coarse and fine chars is shown in Figure 7. Surprisingly the burn-off was faster for the coarse pits. This could be due to a higher volatile content of the starting material which would lead to a higher intercept on the left axis provided enough activation points were determined to permit extrapolation of the burn-off curve back to 0 time. The Burn-off curve for fine particles extrapolated to about 2% whereas its Volatile Matter analysis was 4.3%.

In Figure 8 the screen analyses are shown for the 42 minute composite both before and after abrasion in the abrasion test pan. It is apparent that some fines were generated in the activation process since all the minus 10 mesh material was removed from the char initially. No screen analysis of the raw char was made though this would have been helpful in determining the particle shrinkage. The reduction in <u>median</u> particle diameter upon abrasion shows almost the same degradation as the <u>mean</u> particle diameter.

The Abrasion No. calculated from Median Particle Diameters is 81.9%, slightly higher than the conventional Abrasion No. of 80.65%.

RECOMMENDATIONS

The above data are obviously incomplete due to the limited scope of the project. It should be helpful to more thoroughly compare chars made in the lab and in the plant which are both available. Another composite sample for 50 minutes activation would be helpful in pinning down hardness and "carbontet" data.

It has been suggested that an entire series based on attrition mill-ground pits be conducted to set a standard or target to be met by plant production. Filling out the above program with the inclusion of activation of the muffle-charred material would be helpful in pointing out whether there is a real difference in plant charring capability. It is hoped that this work may be undertaken when the new coarse-ground pits are received.

Respectfully submitted,

Stanton B. Smith, Ph.D.
Principal Research Scientist

TABLE I

MUFFLE FURNACE PYROLYSIS OF COARSELY SIZED PEACH PITS

Rectangular stainless steel food container
N2 purge through single sparger tube, 3L/min.

TEMPERATURES

Controlled furnace temperature

Initial	350°C (662°F)
Final	840°C (1544°F)

Programmed rise rate at 50°C every 15 minutes

Charge temperatures determined by 3 T/C's

Initial	Room Temp.
Final	827°C (1520°F)

CHARGE DATA

Weight & Volume

Initial	3083 g, 5.23 l (as received)
Final Product	863 g, 1.82 l

Densities, Apparent*

Initial	.589/g/ml
Final Product	.474 g/ml

YIELD DATA

By Weight	28.0 % wb
By Volume	34.8 %

* Determined on 500 ml in a 500 ml graduate

TABLE II

ACTIVATION OF PACIFIC CARBONS, INC. COARSE PEACH PIT CHAR

Screened to +10 Mesh, Oven dried (4.3% H_2O before drying) 2" Rotary furnace

	ACTIVATION		PRODUCTS		FEEDSTOCK
Run No:	1	2	Composite 3,4,5,6	Abraded Comp. 3-6	PCI Char +10
Act'n Time min	50	41	42	42	0
Yield %db	49.0	59.6	56.7(Avg)	nd	?
AD** g/ml	.256	.288	.282	nd	.433
IN g/g	1097	880	920	nd	nd
DI DI units	19.7	nd	13.9	nd	nd
CCl_4					
Capacity, %	61.7*	51.6*	46.5	17.6*	nd
Retentivity, %	nd	nd	21.2	23.1	nd
Abrasion No.	-	-	80.65	-	nd
Screen Analysis					
U.S. No.					
+4			10.28	6.29	
4 x 6			49.3	33.03	
6 x 8			31.74	27.94	
8 x 10			6.59	10.68	
10 x 16			0.80	10.88	
16 x 20				2.89	
-20			1.20	8.28	
Mean PD mm			3.606	2.908	
Median PD mm			3.60	2.95	

nd - not determined
* Given additional 1 hr drying @ 140°C
** Determined in 100 ml graduate

FIGURE 1

PYROLYSIS UNIT FOR LARGE MUFFLE FURNACE

Rectangular Stainless-Steel Food Container

with Inert Gas Purging

Volume ca. 5¼ liters

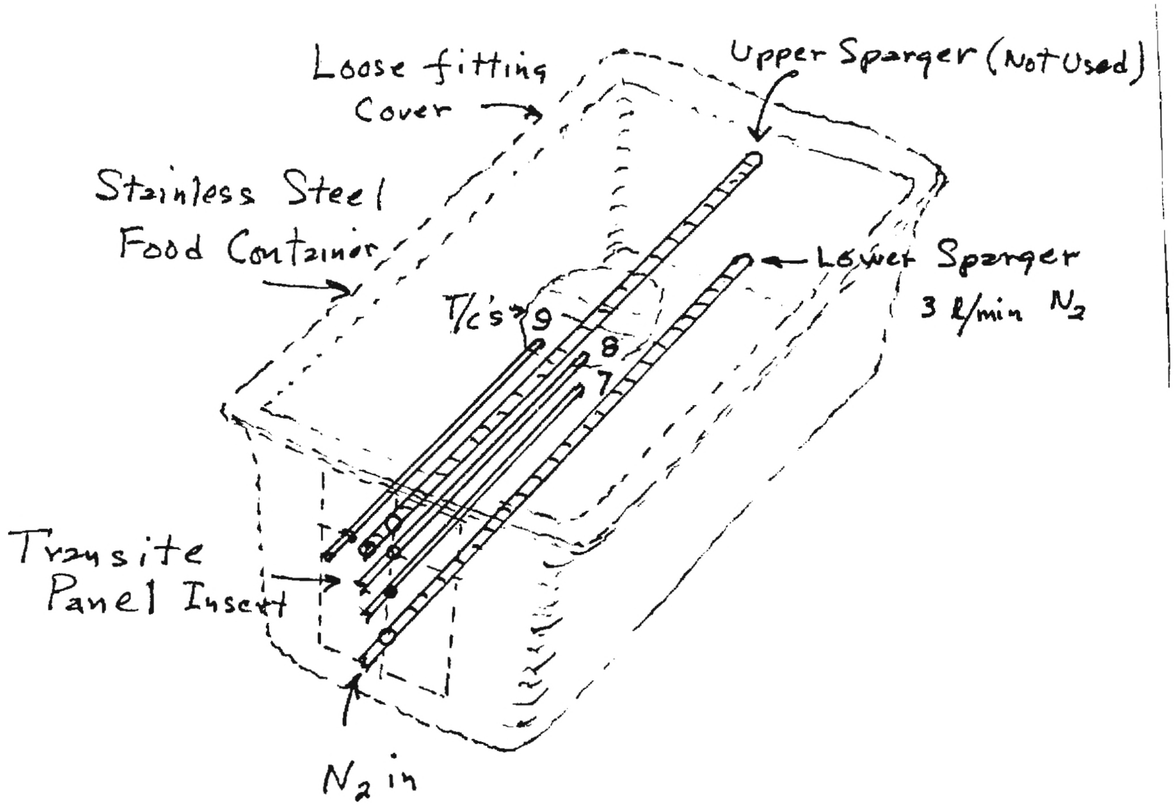

FIGURE 2

THERMOCOUPLE TRACE OF PYROLYSIS RUN
OF COARSE PEACH PITS

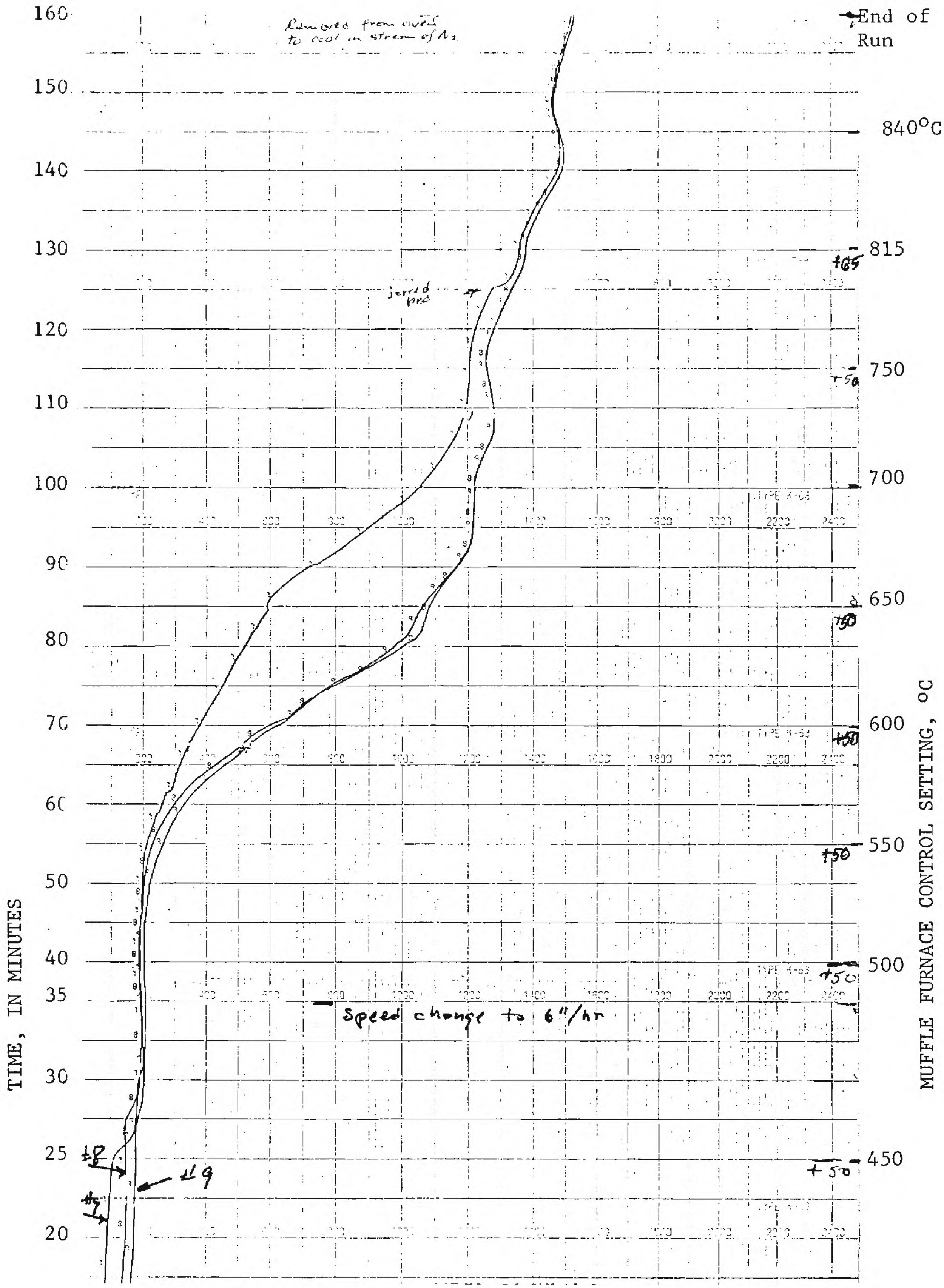

FIGURE 3

ACTIVATION OF COARSE & FINE
CHARRED PEACH PITS
Iodine Nos. & Decolorizing Index
vs. Yield

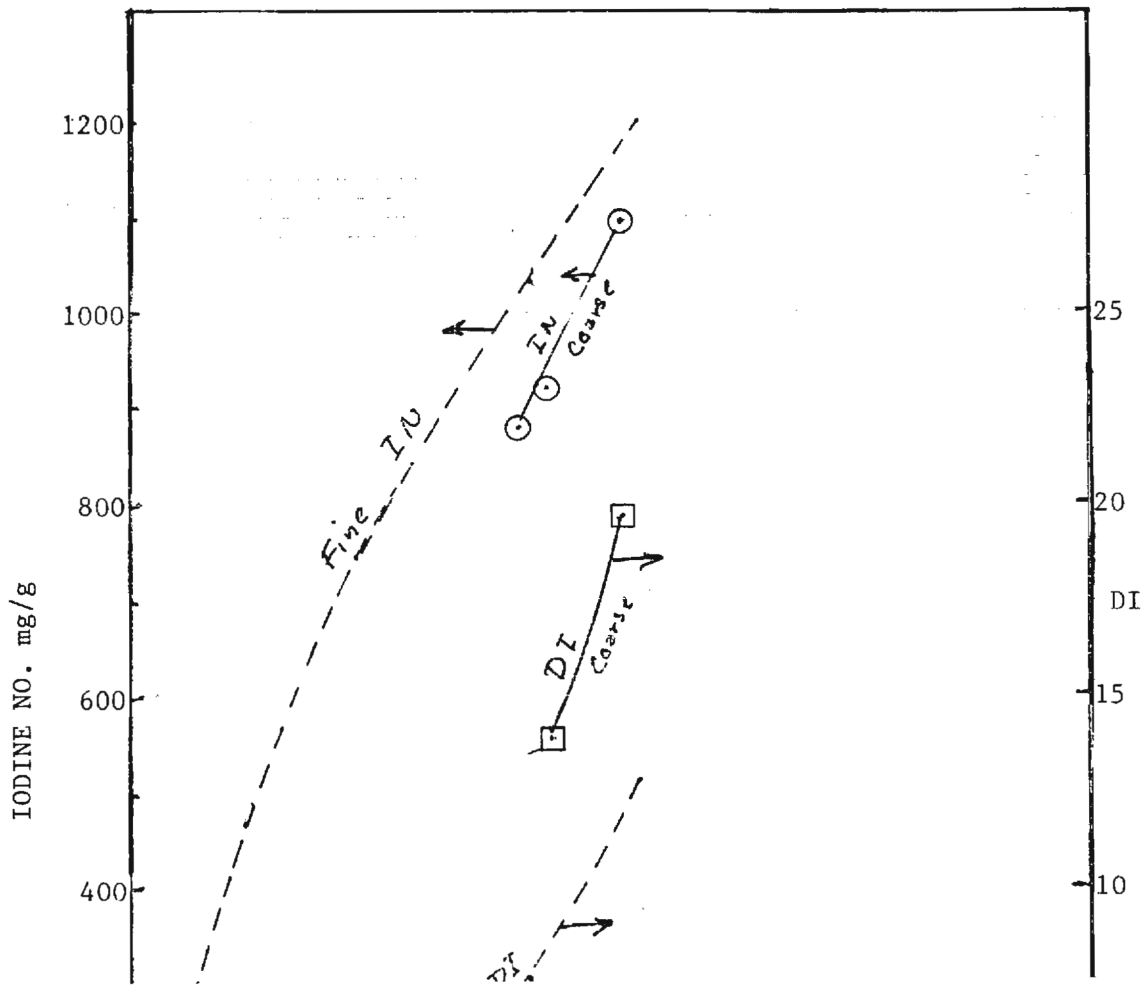

FIGURE 4

ACTIVATION OF COARSE & FINE
CHARRED PEACH PITS
Carbon Tetrachloride Capacity & Retentivity
vs. Yield

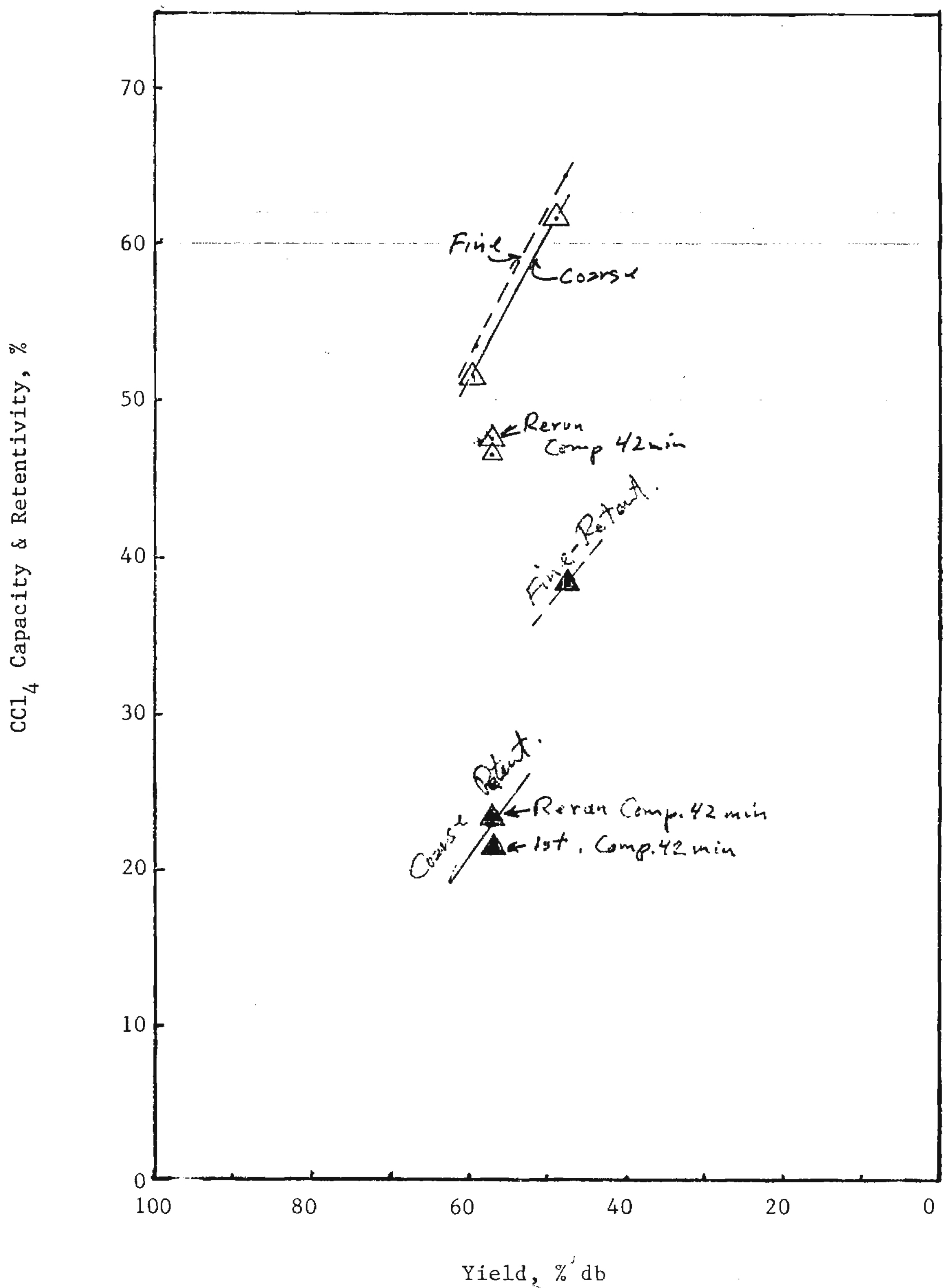

FIGURE 5

DENSITY CHANGES OF SIZED PEACH PITS
DURING CHARRING & ACTIVATION

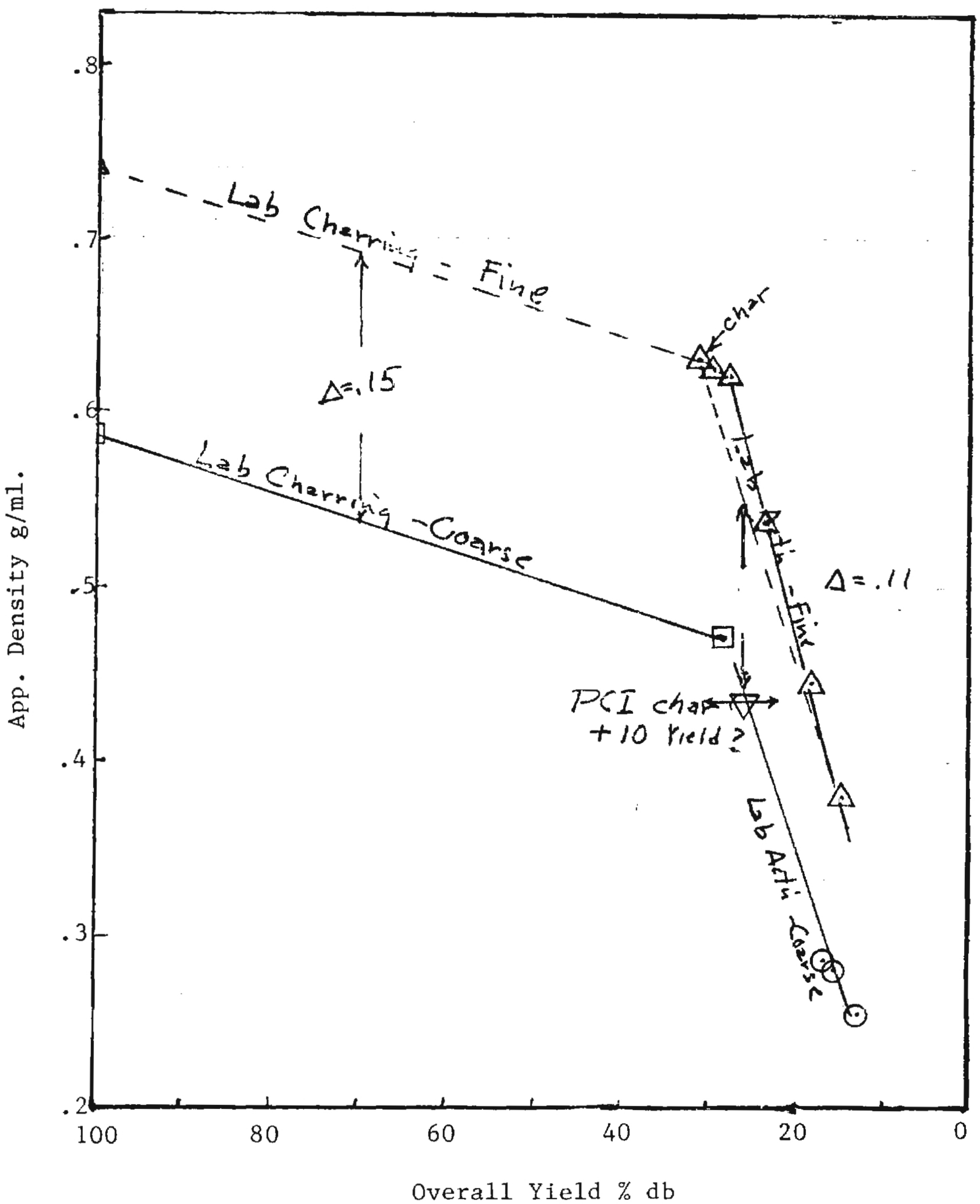

FIGURE 6

DENSITY CHANGES OF SIZED PEACH PITS
DURING ACTIVATION

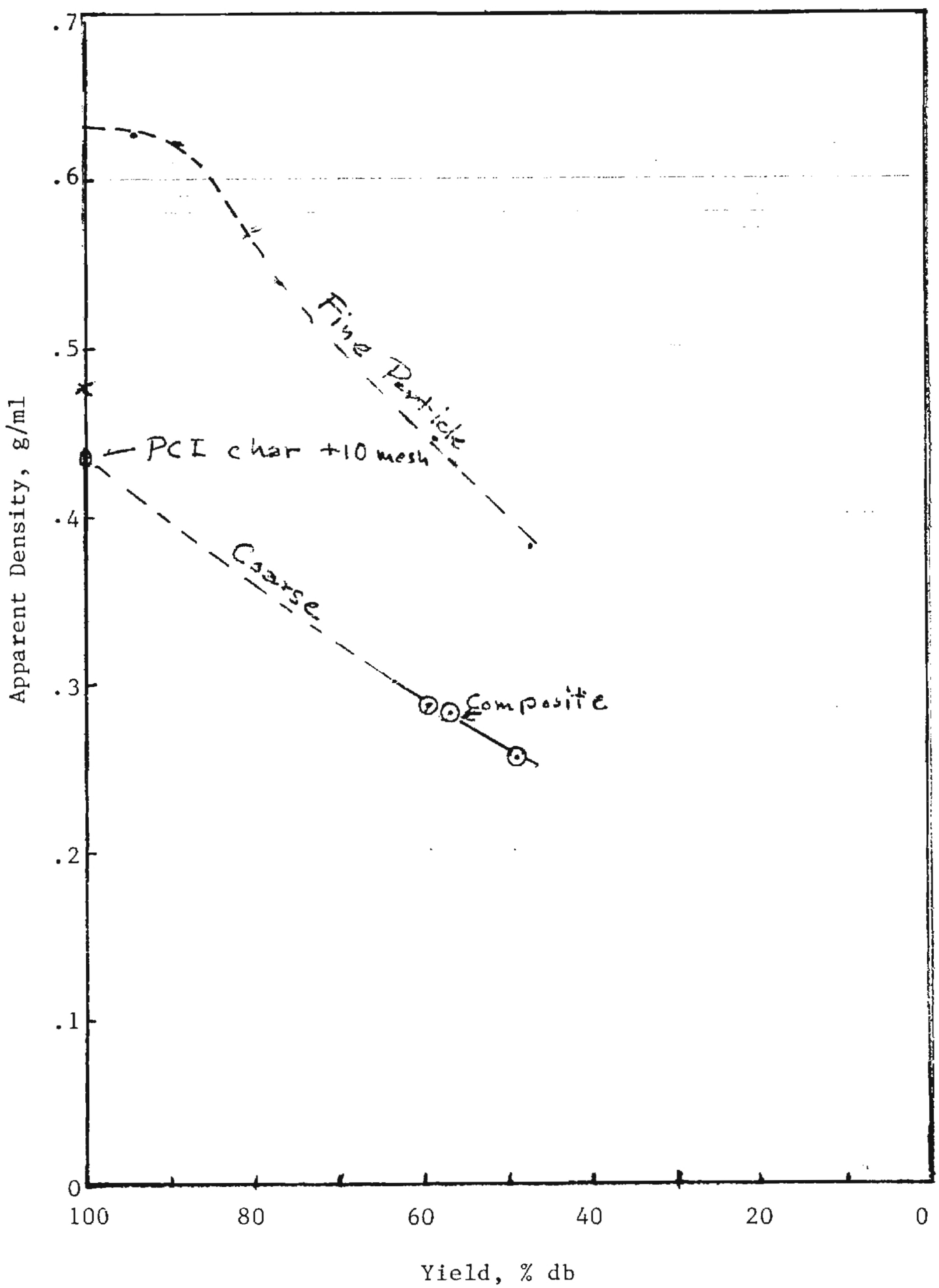

FIGURE 7

BURN-OFF RATE OF PEACH PIT CHARS
2" Rotary Tube Furnace, 50g Charge
$1700^{o}F$, 2 g H_2O/min

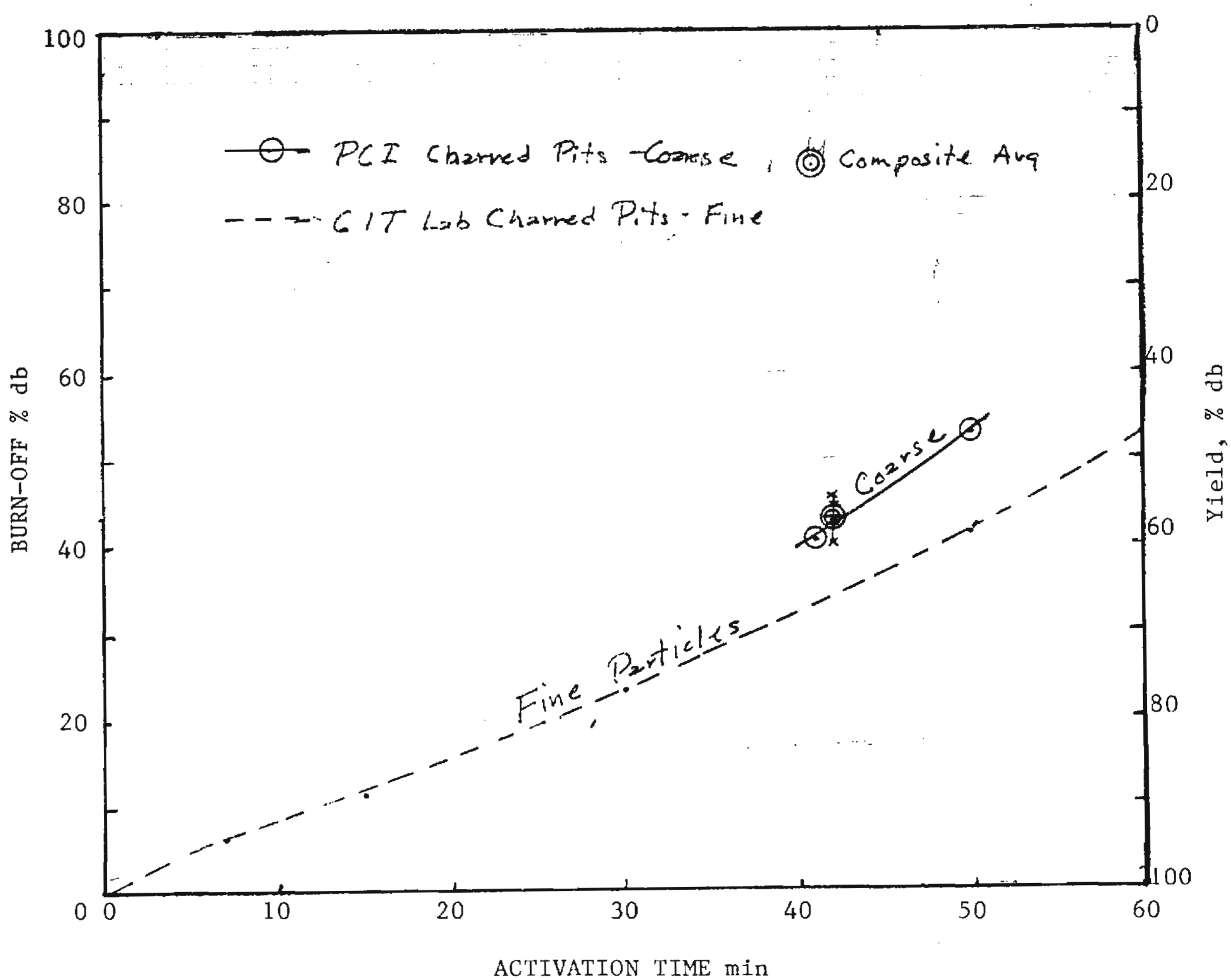

FIGURE 8

PARTICLE SIZE DISTRIBUTION OF

COARSE ACTIVATED PEACH PIT CHAR